



## Phonon limited electronic transport in Pb

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# Phonon limited electronic transport in Pb

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**Abstract.** We present a fully *ab initio* based scheme to compute electronic transport properties, i.e. the electrical conductivity  $\sigma$  and thermopower  $S$ , in the presence of electron-phonon interaction. We explicitly investigate the  $\mathbf{k}$ -dependent structure of the ELIASHBERG spectral function, the coupling strength, the linewidth and the relaxation time  $\tau$ . We obtain a state-dependent  $\tau$  and show its necessity to reproduce the increased thermopower for temperatures below the DEBYE temperature, without accounting for the phonon-drag effect. Despite the detailed investigations of various  $\mathbf{k}$ - and  $\mathbf{q}$ -dependencies, the presented scheme can be easily applied to more complicated systems.

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## 1. Introduction

The interaction between fermions and bosons plays an important role in solid state physics and gives rise to many fundamental phenomena. While conventional phonon-mediated superconductivity is one of the most studied aspects in many-particle physics, recently the impact of electron-phonon (EP) coupling on carrier lifetimes [3, 36, 31], band renormalization [5, 37], phonon-assisted absorption [34, 38], relaxation dynamics of excited carriers [6], electronic mobilities [21, 15] and thermoelectric properties [49, 28] got increased focus. The demand for a consistent theoretical description of these phenomena led to many methodological improvements in recent years [14, 40] and enables computationally feasible ways to calculate and predict electron-phonon mediated material properties. As the archetype strong-coupling superconductor, Pb has been the material of choice in various theoretical studies of electron-phonon coupling properties [45, 46, 17]. Within this manuscript we introduce an in-depth study of the electron-phonon interaction in fcc bulk Pb. Introducing our method based on density functional perturbation theory and improved tetrahedron interpolations we discuss anisotropic  $\mathbf{k}$ - and  $\mathbf{q}$ -dependent material properties, e.g. electron-phonon coupling parameter, linewidths and lifetimes as well as state-dependent band renormalizations. Based on the evaluation of the complex electron-phonon self energy we solve the Boltzmann transport equation in relaxation time approximation and elaborate details on the temperature-dependence of the electrical conductivity and thermopower within different approximations to the scattering rates. An enhancement of the thermopower at low temperatures due to the state-dependency of the relaxation times could be unveiled. More general we find, that simple single-sheeted FERMI surfaces will yield smaller electron-phonon-coupling, i.e. larger relaxation times, compared to complicated multi-sheeted ones. Our in-depth analysis of an electron-phonon driven material, such as Pb, might help to gain a more systematical understanding of how to predict material properties influenced by electron-phonon-coupling.

## 2. Methodology

The electron and phonon properties were calculated within the framework of density functional perturbation theory as implemented in the Quantum Espresso package [12]. We investigate Pb with the lattice constant  $a_{lat} = 9.2 \text{ a.u.}$  and use a scalar-relativistic norm-conserving pseudopotential with the Perdew-Zunger exchange correlation functional and the local density approximation<sup>‡</sup>. The evaluation of the electron-phonon interaction is based on the el-ph matrix elements, which are first calculated on a coarse  $18 \times 18 \times 18$  k-grid and  $8 \times 8 \times 8$  q-grid and afterwards wannier-interpolated to finer grids using Wannier projections as implemented within the EPW code [40]. The interpolation at each initial electronic state  $\mathbf{k}$  is performed with the interaction of at least 200'000 phonon states  $\mathbf{q}$ .

The effectiveness of phonons with energy  $\hbar\omega$  to scatter electrons can be expressed by means of the, *a priori* state-dependent, ÉLIASHBERG spectral function within the

<sup>‡</sup> We note that Pb should be treated in a fully-relativistic description due to its large spin-orbit coupling but the methodical framework we present is not restricted to a special type of pseudopotential and relativistic effects can be added. The impact of these effects on properties determined by electron-phonon (el-ph) interaction is discussed in several papers [8, 46] and do not change our results qualitatively.

quasi-elastic assumption

$$\alpha^2 F_{\mathbf{k}n}(\omega, \epsilon_{\mathbf{k}n}) = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q}\nu m} \delta(\omega - \omega_{\mathbf{q}\nu}) \left| \mathbf{g}_{\mathbf{k}'m, \mathbf{k}n}^{\mathbf{q}\nu} \right|^2 \delta(\epsilon_{\mathbf{k}n} - \epsilon_{\mathbf{k}'m}) \quad (1)$$

where  $\omega_{\mathbf{q}\nu}$  is the phonon frequency of state  $\mathbf{q}$  in mode  $\nu$ ,  $N_{\mathbf{q}}$  is the number of  $\mathbf{q}$  points,  $\epsilon_{\mathbf{k}n}$  is the energy of an electron in initial state  $\mathbf{k}$  and  $n$ -th band and  $\mathbf{k}'$  being the final state given by  $\mathbf{k} + \mathbf{q}$ . The kernel of the ÉLIASHBERG spectral function are the electron-phonon matrix elements

$$\mathbf{g}_{\mathbf{k}'m, \mathbf{k}n}^{\mathbf{q}\nu} = \sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}\nu}}} \langle \Psi_{\mathbf{k}n+\mathbf{q}\nu} | \partial V_{\mathbf{q}\nu} | \Psi_{\mathbf{k}n} \rangle \quad (2)$$

which manifest the interaction of the initial ( $\Psi_{\mathbf{k}n}$ ) and final ( $\Psi_{\mathbf{k}n+\mathbf{q}\nu}$ ) electronic states via a phonon ( $\mathbf{q}\nu$ ). Within  $\partial V_{\mathbf{q}\nu}$  is the first-order derivative of the Kohn-Sham potential with respect to the atomic displacements induced by a phonon mode  $\nu$  with frequency  $\omega_{\mathbf{q}\nu}$ .

Integration of the ÉLIASHBERG spectral function then directly leads to the electron-phonon coupling constant

$$\lambda = 2 \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \quad (3)$$

and the phonon-induced electron linewidth

$$\Gamma_{\mathbf{k}n}(\epsilon_{\mathbf{k}n}) = 2\pi \int_0^\infty d\omega \alpha^2 F_{\mathbf{k}n}(\omega, \epsilon_{\mathbf{k}n}) \mathcal{H}(b, f) \quad \text{with} \quad (4)$$

$$\mathcal{H}(b, f) = [1 + 2b(\omega) + f(\epsilon_{\mathbf{k}n} + \hbar\omega) - f(\epsilon_{\mathbf{k}n} - \hbar\omega)]$$

and  $b$  and  $f$  being the BOSE-EINSTEIN and FERMI-DIRAC distribution functions, respectively. The inverse linewidth is proportional to the el-ph relaxation time  $\tau_{\mathbf{k}n} = \hbar/\Gamma_{\mathbf{k}n}$ . We note, that the corresponding electron-induced phonon linewidths  $\Gamma_{\mathbf{q}\nu}(\omega)$  can be easily obtained by summing over  $\mathbf{k}$  instead of  $\mathbf{q}$  in eq. 1.

An enhanced interest of the influence of el-ph interactions on  $\mathbf{k}$ - and energy-dependent electron properties,  $\mathbf{q}$ -dependent phonon properties as well as transport properties, especially in 2D-materials [19, 36, 29, 26, 15] and bulk semi-conductors [39, 3, 48, 24], came up recently. A quantity of major interest in transport calculations is the transport relaxation time  $\tau_{\mathbf{k}n}^{\text{tr}}$ . It can be calculated by adding an efficiency factor

$$1 - \frac{\mathbf{v}_{\mathbf{k}n} \cdot \mathbf{v}_{\mathbf{k}'m}}{|\mathbf{v}_{\mathbf{k}n}| |\mathbf{v}_{\mathbf{k}'m}|} \quad (5)$$

to eq.(1), which accounts for the *scattering in* term in the iterative solution of the Boltzmann transport equation and appears like a change of the absolute value of the velocity during the scattering process. The denominator is usually approximated by  $|\mathbf{v}_{\mathbf{k}n}|^2$ . This is reasonable in simple metals e.g. lithium or sodium possessing isotropic spherical FERMI surfaces but does not hold for lead or even more sophisticated systems, which provide complex and anisotropic FERMI surfaces. The impact of the different approximations to the efficiency factor is shown in detail in the Appendix.

An equivalent way of calculating the relaxation time is given by solving a linearized BOLTZMANN equation. We note, that the *scattering in* term is usually approximated by the efficiency factor Eq. 5. Accounting for the *scattering out* term only, would correspond to the relaxation time approximation (RTA). A full solution of the Boltzmann equation would be carried out straight-forwardly by applying an

iterative scheme as introduced earlier for the solution of the phonon Boltzmann equation [35]. Other methodologies to the full solution of the Boltzmann equation ground on variational approaches based on trial functions [16, 32] or variational approaches based on conjugated gradients [11]. It has been shown in the past, that the suggested solution approaches can be applied to solve the electron, as well as the phonon Boltzmann equation [25, 24]. Recently, results solving the full BOLTZMANN equation were published [24, 9]. Within it is shown that applying the full iterative solution accounting for el-ph scattering instead of a relaxation time approximation or an approximation including the efficiency factor, does not change the result noticeably for several studied metals and semiconductors. Nevertheless, this might not be valid for every system. Within the manuscript, the transport quantities  $\tau^{\text{tr}}$ ,  $\lambda^{\text{tr}}$  and  $(\alpha^2 F_{\mathbf{k}})^{\text{tr}}$  explicitly account for the *scattering in* term via the efficiency factor, while the latter is neglected for the spectroscopic counterparts  $\tau$ ,  $\lambda$  and  $(\alpha^2 F_{\mathbf{k}})$ .

Besides the linewidth and relaxation time, which are linked to the imaginary part of the complex electron self-energy  $\Sigma(\epsilon_{\mathbf{k}n}, T) = \Sigma'(\epsilon_{\mathbf{k}n}, T) + i\Sigma''(\epsilon_{\mathbf{k}n}, T)$  via  $\Gamma_{\mathbf{k}n}(T) = 2\Sigma''_{\mathbf{k}n}(T)$ , the renormalization of the electronic states, being mainly connected to the real part of  $\Sigma$ , is less investigated in transport calculations. However, it may play an important role at low temperatures due to its large influence on the bandstructure around the FERMI energy. The renormalized energy  $\bar{\epsilon}_{\mathbf{k}n}$  of the state  $\mathbf{k}$ , as maximum of the spectral function  $A(\mathbf{k}, T)$ , is given by

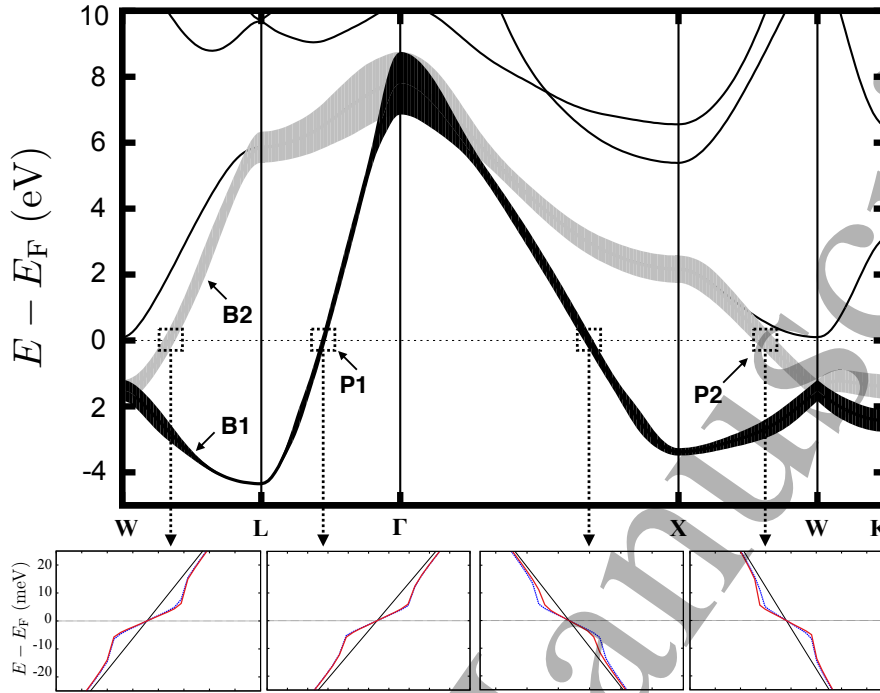
$$\bar{\epsilon}_{\mathbf{k}n} = \epsilon_{\mathbf{k}n} + \Sigma'(\bar{\epsilon}_{\mathbf{k}n}, T) \quad (6)$$

Practically, one uses a modified KRAMERS-KRONIG relation to obtain the real part of the self-energy from the imaginary part [23].

### 3. Results

The scalar-relativistic band structure of Pb shown in figure 1 resembles previous calculations[51, 17, 46]. Deviations from experiments occur due to spin-orbit interaction and are found primarily at the crossing points at W, L,  $\Gamma$ , on the high-symmetry line  $\overline{XW}$  leading to avoided crossings. Since these regions are not close to the FERMI energy the influence on transport properties, like electrical conductivity or thermopower, is rather small at moderate temperatures.

The effect of the el-ph interaction onto the bare single-particle states is shown as superimposed linewidth and renormalization (inset fig. 1). The scattering of an electron with a phonon leads to a finite lifetime and linewidth of the electronic state. The absolute value of the linewidth depends on the interaction strength and the possible scattering phase space. The latter is determined by an energy conservation,  $\epsilon_{\mathbf{k}'m} = \epsilon_{\mathbf{k}n} \pm \hbar\omega_{\mathbf{q}\nu}$ , and momentum conservation,  $\mathbf{k}'_m = \mathbf{k}_n \pm \mathbf{q}_\nu$ . Generally the phase space can be rather small in terms of the electronic energy scale, as the highest phonon energies are typically in the order of 10-100 meV, depending on whether metals [43] or semiconductors [13] are in focus. Therefore, sampling the BRILLOUIN zone sufficiently is demanding. Consequently, it is complemented by the powerful Wannier interpolation scheme. The renormalization of an electronic state due to el-ph interaction results in an effective gain or loss of the electron energy, related to its position relative to  $E_F$ . The renormalization shown in the insets is done with the ordinary  $\mathbf{k}$ -independent ÉLIASHBERG spectral function, where we assumed an isotropic renormalization for all electronic states (dashed blue line), and the  $\mathbf{k}$ -dependent spectral function (solid red line). In both cases characteristic *kinks* appear

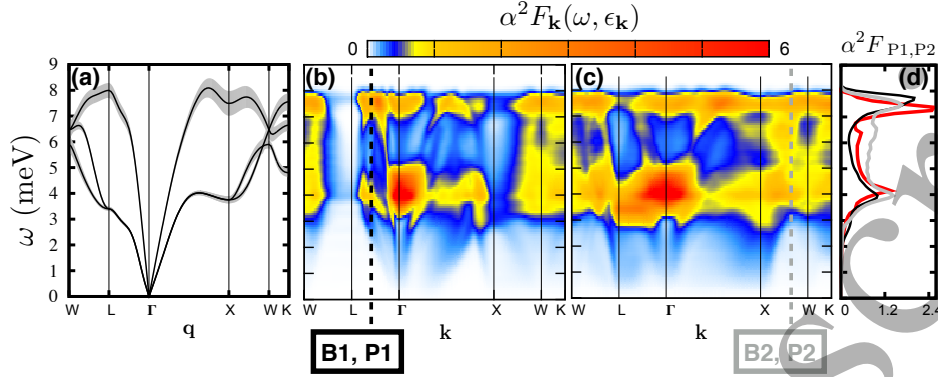


**Figure 1.** Calculated band structure of Pb within the scalar-relativistic framework. The width of the superimposed shaded areas onto the electronic states of band B1 and B2 is related to the magnitude of the  $\mathbf{k}$ -dependent linewidth at 300 K shown in figure 3(b). The values for the states P1 and P2 are 211 meV and 304 meV. The insets show the renormalized bandstructures around the Fermi energy at 10 K. The renormalization is done with the isotropic  $\mathbf{k}$ -independent (dashed blue line) and the  $\mathbf{k}$ -dependent ÉLIAHBERG spectral function (solid red line). The *kinks* appear around the maximal phonon energy.

around  $E = E_F \pm \omega_{\max}$ , with  $\omega_{\max} \approx 8\text{meV}$  being the largest phonon frequency in lead. This leads to reduced velocities and an increased density of states (DOS) inside the window and to enhanced velocities and lowered DOS outside. While the isotropic approximation is reasonable at certain  $\mathbf{k}$  points (around P1), it usually under- or overestimates the renormalization effect (around the crossing along  $\bar{\Gamma}\text{X}$  and around P2). With increasing temperature the *kinks* are disappearing and the influence on the states is negligible. For electronic states far away from  $E_F$ , the possibility to absorb or emit a phonon is small and there is no significant influence of the el-ph interaction onto the electronic bands anymore no matter how small or large the temperature is.

Figure 2(a) shows the calculated phonon dispersion of bulk Pb. A comparison with experimental data and other calculations including spin-orbit interaction, reveals differences to the scalar-relativistic calculation [8, 17]. Basically three features are missing. First, mode softening at certain points in the BRILLOUIN zone is not observed, most pronounced at X. Second, the absolute value of the phonon bandwidth is  $\approx 10\%$  to large. Third, KOHN anomalies, e.g. along the  $\bar{\Gamma}\text{K}$ -line, due to FERMI surface nesting are not accounted for. Overall these features result in an enlarged el-ph coupling parameter and thus the relaxation times presented in this work will slightly overestimate possible experimental findings. Superimposed onto each mode is the





**Figure 2.** (a) Phonon dispersion curves with superimposed linewidths due to el-ph interaction. The maximum width corresponds to  $\sim 32\text{meV}$ . (b), (c)  $k$ -dependent ÉLIASHBERG spectral function  $\alpha^2 F_k(\omega, \epsilon_k)$  along the high-symmetry line given in figure 1 for the bands B1 and B2. The colour-code is related to the values of  $\alpha^2 F_k$ . The states P1 and P2 are highlighted as dashed black and grey lines. (d)  $\alpha^2 F_k$  of state P1 (black) and P2 (grey) on the FERMI surface. The contributions to the spectral function in P1 arise almost entirely from high-energy phonons, while the phonons involved in the coupling at P2 show a wider energy distribution. The red line shows the FERMI surface averaged spectral function usually used when evaluating spectral and transport properties.

phonon linewidth

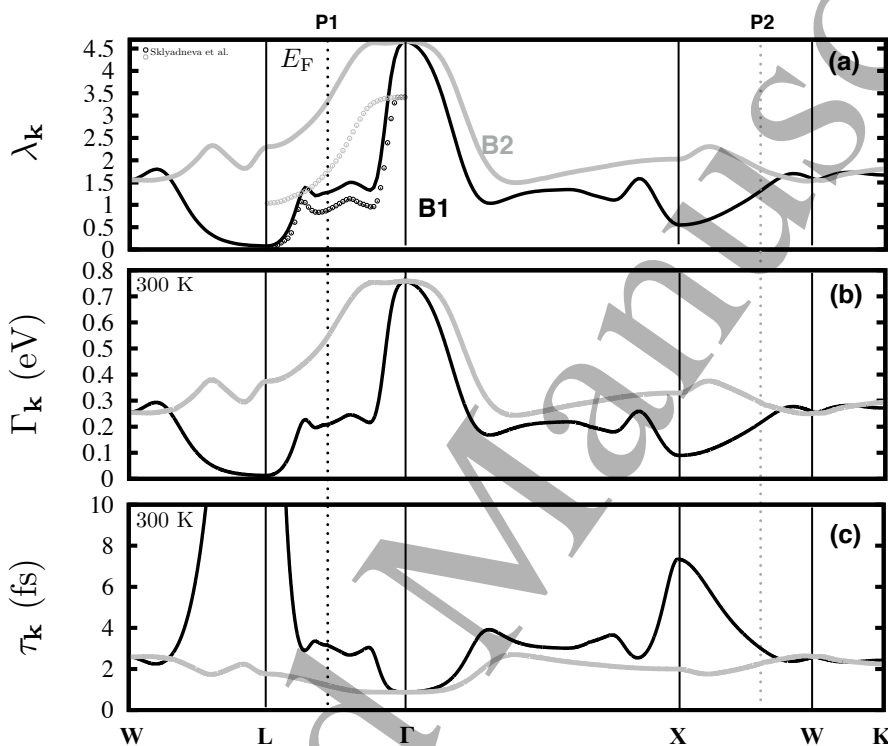
$$\gamma_{q\nu} = 2\pi\omega_{q\nu} \sum_{kmn} \left| g_{\mathbf{k}'m, \mathbf{k}n}^{q\nu} \right|^2 \delta(\epsilon_{\mathbf{k}'m} - E_F) \delta(\epsilon_{\mathbf{k}n} - E_F) \quad (7)$$

It can be seen that the linewidth is large for high-energy phonons and drops to zero with  $\omega \rightarrow 0$ . The renormalization of the phonon modes is already included within density functional perturbation theory (DFPT) since the real part of the phonon self-energy in the static limit equals the contribution to the dynamical matrix, which arises from the variation of the electron density. Hence, calculating phonon frequencies within DFPT already includes the renormalization due to the real part of the phonon selfenergy.

The  $k$ -dependent ÉLIASHBERG spectral function of the electronic states along the high-symmetry line given in fig. 1 is shown in fig. 2(b) and (c) for bands B1 and B2. These quantities serve as direct input for the calculation of the relaxation times. First of all, the shape of each  $\alpha^2 F_k$  is quite similar compared to the isotropic FERMI surface averaged ÉLIASHBERG function in Pb (red line in fig. 2(d)). Two peaks can be seen, more or less distinct from each other. One originates from high-energy phonons with approximately 7-8 meV and the other one arises from non-dispersive phonons around 3-4 meV. This pattern can be observed even at the L point in the band B1, where the scattering phase space is almost vanishing. The highest values of  $\alpha^2 F_k$  are found around  $\Gamma$ . Here, the electronic bandstructure favours the coupling to phonons with wavevector  $q$  along the  $\Gamma X$  direction. Since the dispersion of these phonons is rather flat nearby 3-4 meV, the contribution to  $\alpha^2 F_k$  is large. The states P1 and P2, lying on the FERMI surface are highlighted in fig. 2(c) and (d) with dashed black and grey lines and are displayed separately in figure 2(d). As mentioned before, both ÉLIASHBERG functions provide the two-peak-structure. While  $\alpha^2 F_{P1}$  is dominated



by the low-dispersive mid- and high-energy phonons, the contributions to  $\alpha^2 F_{P2}$  are distributed over the energy range. Here, phonons are more dispersive and have larger velocities, heavily impacting the ÉLIASHBERG function. In both cases the coupling to phonons with an energy less than 2 meV is weak. These properties of the points P1 and P2 are characteristic for the anisotropy of the ÉLIASHBERG spectral function, the coupling constant, the linewidth and the relaxation time on the FERMI surface discussed within this manuscript.



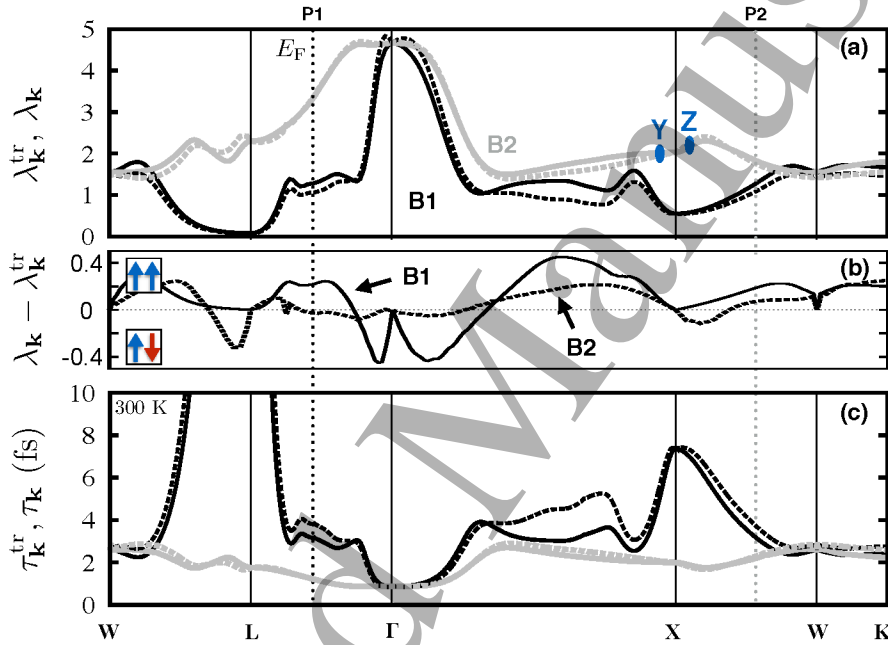
**Figure 3.** Various  $k$ -dependent el-ph properties. The vertical dotted line indicate the crossing of the states P1 and P2 of the FERMI energy of the bands B1 (black) and B2 (grey). All quantities in (a)-(c) were calculated via an integration over the ÉLIASHBERG spectral function given in figure 2(b) and (c). (a) Electron-phonon coupling parameter. (b) Linewidth at 300K. (c) Spectral electron-phonon relaxation time obtained from the linewidths in (b). At 300K,  $\tau_k$  is about 3.15fs and 2.15fs in P1 and P2, respectively.

A certain quantity obtained from the ÉLIASHBERG function is the  $k$ -dependent coupling constant  $\lambda_k$ , which is shown in fig. 3(a). The calculated values along the FL line are qualitatively in good agreement with data from Sklyadneva *et al.* [46]. They show the same  $k$ -dependency for B1 as well as for B2. The coupling constants  $\lambda$  for P1 and P2 are 1.30 and 1.79. The FERMI surface averaged coupling strength is 1.35, which is higher than reported by Sklyadneva *et al.* but still in good agreement with other published results based on a scalar-relativistic treatment of lead [30, 10, 1]. At higher temperatures, the factor  $[1 + 2b(\omega) + f(\epsilon_{kn} + \omega) - f(\epsilon_{kn} - \omega)]$  in eq. (4) is almost determined by  $1/\omega$  and therefore the shape of the linewidth (fig. 3(b)) and the coupling strength are quite similar to each other.  $\Gamma_k$  is 0.211 eV

## Phonon limited electronic transport in Pb

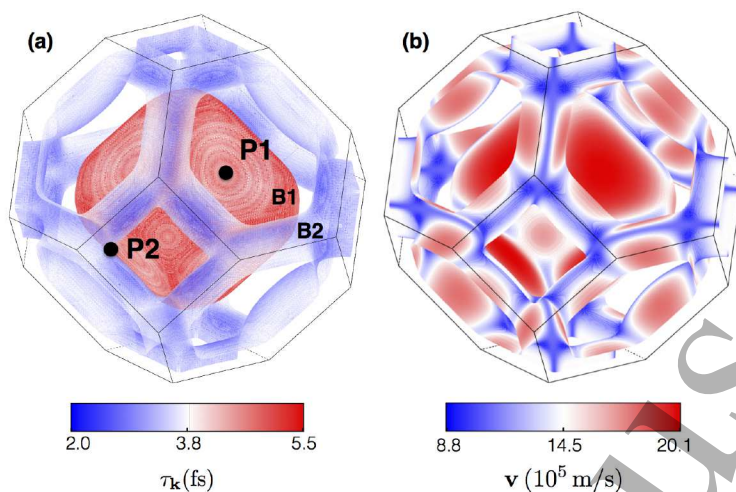
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and 0.295 eV for P1 and P2, respectively. The inverse linewidth gives rise to the relaxation time, shown in fig. 3(c). The largest value can be observed for B1 at L since the scattering phase space is small and nearly no coupling between electrons and phonons occurs. Conversely,  $\tau$  exhibits the smallest value at  $\Gamma$ , because of the large coupling between electrons and phonons. The anisotropy of the ÉLIASHBERG function at the FERMI energy yields relaxation times of 3.15 fs and 2.15 fs for P1 and P2. The FERMI surface averaged relaxation time within the high-temperature limit,  $\tau(E_F) = \hbar/2\pi k_B \lambda T$ , at  $T = 300\text{K}$ , when the temperature is much higher than the DEBYE temperature, is 3.00 fs. Despite the larger  $\tau$  at P1, scattering in the outer FERMI sheet (B2) is the dominant part (c.f. Fig. 5(a)). The latter is related to the topology of the FERMI surface and will be discussed subsequently.



**Figure 4.** Comparison of the  $\mathbf{k}$ -dependent transport properties with its spectroscopical counterparts. The graphical layout is the same as in figure 3. (a) Coupling constants  $\lambda_k^{\text{tr}}$  (dashed lines) and  $\lambda_k$  (solid lines). Y and Z are highlighted k-points which are discussed in more detail within the main text. (b) Difference  $\lambda_k - \lambda_k^{\text{tr}}$ , at some  $\mathbf{k}$  points either forward- (positive,  $\uparrow\uparrow$ ) or backward-scattering (negative,  $\uparrow\downarrow$ ) is favoured. (c) Relaxation times  $\tau_k^{\text{tr}}$  (dashed lines) and  $\tau_k$  (solid lines) at 300 K.

The spectroscopical properties discussed so far are of minor interest when calculating transport properties. For the latter one needs to include the efficiency factor given in eq. (5). The overall trend, obtained by the spectroscopical properties, does not change drastically when taking the efficiency factor into account (see fig. 4(a), (c)). Nevertheless, certain  $\mathbf{k}$  points favour either effective forward- ( $\uparrow\uparrow$ ) or backward-scattering ( $\uparrow\downarrow$ ), depending on the sign of the function  $\lambda_k - \lambda_k^{\text{tr}}$ , which is given in fig. 4(b). Which one is favoured is usually not predictable *a priori* and depends on the geometry of the FERMI surface, the coupling strength, or on a delicate mixture of both. A detailed analysis of the scattering events would be necessary and will be exemplary



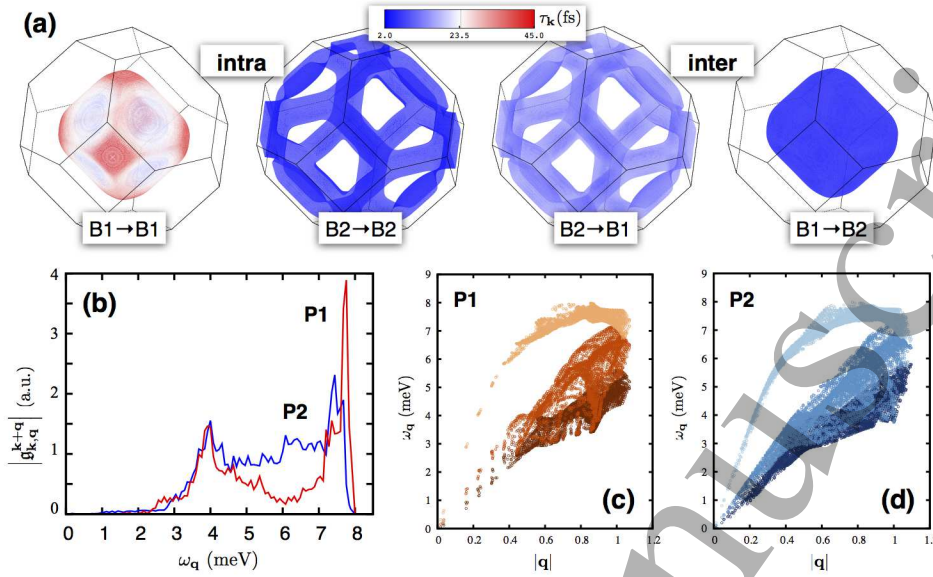
**Figure 5.** (a) FERMI surface of Pb showing the  $\mathbf{k}$ -dependent electron-phonon relaxation times  $\tau_{\mathbf{k}}$  at  $T = 300\text{K}$  superimposed onto the two sheets of the FERMI surface.  $\tau_{\mathbf{k}}$  is obtained by the solution of the BOLTZMANN equation within the relaxation time approximation. The relaxation time is almost doubled in the inner sheet (B1) indicating a less efficient electron-phonon coupling compared to the outer sheet (B2).  $\tau_{\mathbf{k}}$  in P1 and P2 is about 4.60fs and 3.27fs, respectively. (b) FERMI surface with the superimposed FERMI velocities.

done at the  $\mathbf{k}$  points Y and Z of the band B2 around the high-symmetry point X. It turns out that the efficiency factor decreases (increases)  $\alpha^2 F_{\mathbf{k}}$  at lower phonon energies at Y (Z) but keeps  $\alpha^2 F_{\mathbf{k}}$  relatively unaffected at higher energies. Hence, the resulting transport coupling constant is smaller (larger) and forward (backward)-scattering is favoured. The decrease of  $\lambda_{\mathbf{k}}$  due to the efficiency factor at Y is related to the geometry of the FERMI surface only, which can be seen in a constant coupling approximation. This is not the case at Z, where the coupling strength itself is more important than the geometry of the FERMI surface. Directly at the high-symmetry points,  $\lambda_{\mathbf{k}}^{\text{tr}}$  equals  $\lambda_{\mathbf{k}}$  because of the vanishing velocity at the zone boundaries.

As mentioned before, on average the transport relaxation time differs only slightly from its spectroscopical counterpart. However the changes in  $\mathbf{k}$ -space can be substantially.  $\tau^{\text{tr}}$  is about 3.81 fs at P1 and 2.32 fs at P2, which amounts to an increase of 21% and 8% compared to  $\tau$ .

After the discussion of  $\mathbf{k}$ -dependent properties throughout the BRILLOUIN zone at arbitrary energies in the first part, we now want to look at the specific  $\mathbf{k}$ -resolved structure of the relaxation time at the FERMI energy. Hence, we start from a dense mesh with more than 40'000  $\mathbf{k}$  points in the irreducible part of the BRILLOUIN zone and extract  $\mathbf{k}$  points at the FERMI surface with an adaptive tetrahedron method[50]. We end up with a total number of 460'000 points at the whole surface, which are paired with a dense phonon mesh of 2.2 million  $\mathbf{q}$  points in the full BRILLOUIN zone to ensure convergence of the transport properties.

Figure 5(a) shows the FERMI surface of Pb with the superimposed  $\tau_{\mathbf{k}}$ . The relaxation time of the inner sheet (B1) is always larger than that of the outer sheet (B2) and hence the averaged relaxation time  $\bar{\tau}$  of the inner sheet is 30% larger. The latter *a priori* would make the usage of two constant relaxation times in transport calculations



**Figure 6.** (a) Contributions to  $\tau_k$  arising from intra- and interband transitions. Shown are the initial states. For both transition types, scattering at/to the inner sheet (B1) results in larger relaxation times. The Fermi surface averaged  $\tau_k$  is dominated by the scattering at/to the outer sheet (B2). (b) Electron-phonon matrix elements plotted versus the corresponding phonon energies for P1 and P2 shown in fig. (5). The latter one exhibits an uniform and in total larger electron-phonon coupling strength, which explains the smaller relaxation time. (c,d) Phonon energies versus absolute momentum for phonons being involved into the coupling from the initial states P1 and P2. Each color corresponds to one phonon mode.

feasible. The overall structure of  $\tau_k$  is anisotropic throughout the Brillouin zone, which can be related to the topology of the Fermi surface itself. A certain initial state is coupled by different phonons to a whole set of final states, which is shown in fig. 6(c) and (d). Since the Fermi surface is much more anisotropic around P2 than P1 and both bands are close to each other, the variety of the momenta of the coupled phonons is larger in the initial state P2. For example, only a few phonons with small wave vectors couple to P1, because its surrounding favours only coupling in a certain direction. Therefore, a simple Fermi surface could partially act as a phonon filter §. Besides the geometrical aspects, the  $q$ -dependent coupling strength (fig. 6(a)) shows two distinct peaks for P1 and is more uniform for P2, which coincides with the ÉLIASHBERG spectral function (see fig. 2(d)). Decomposing the relaxation time into contributions from intra- and interband scattering, one can see that  $\tau_{E_F}$  is dominated by transitions B1→B2 and B2→B2 (fig. 6(b)). Large relaxation times from transitions B1→B1 and B2→B1 are suppressed as one needs to add up the scattering rates of all transitions instead of the scattering times to account for MATTHIESEN'S rule. A comparison of the intraband transitions indicates that a simple single-sheeted Fermi surface exhibits larger relaxation times than complicated multi-sheeted ones. In the case of Pb the enhancement compared to  $\bar{\tau}$  is up to 600% for the averaged values  $\bar{\tau}_{B1}^{\text{intra}}$  and  $\bar{\tau}_{B2}^{\text{intra}}$ .

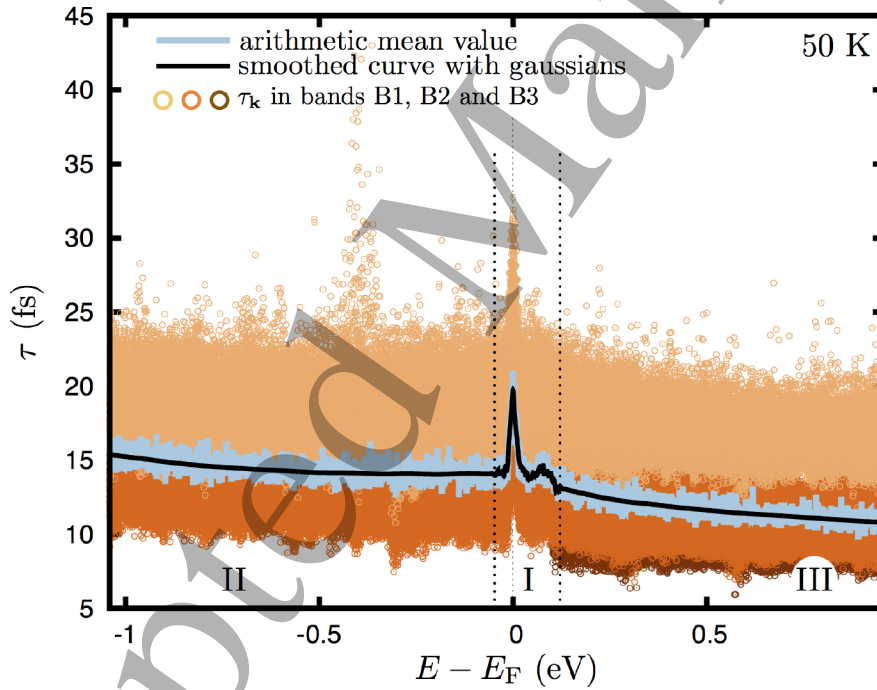
§ Additional figures adding to this discussion can be found in the Appendix.



We note, that there is probably no obvious qualitative correlation between the carrier velocity  $\mathbf{v}_{\mathbf{k}}$  of an initial state and its relaxation time  $\tau_{\mathbf{k}}$  as one might suspect from recent results found for noble metals by Mustafa *et. al*[33]. The relaxation time of a free electron in the Drude model is given by

$$\tau_D = \frac{m^*}{ne^2\rho} \quad , \quad (8)$$

with the resistivity  $\rho$ , carrier density  $n$  and effective mass  $m^*$ . The latter is indirect proportional to the velocity  $m^* \propto v^{-1}$ , which transfers directly to the relaxation time yielding  $\tau_{\mathbf{k}} \propto (\mathbf{v}_{\mathbf{k}})^{-1}$  for a spherical FERMI surface. Surprisingly, this is partially valid in lead, since scattering from an initial state at the inner simple FERMI sheet (B1) shows an indirect proportionality between the relaxation time and the velocity as well. On the other hand,  $\tau_{\mathbf{k}}$  is direct proportional to  $\mathbf{v}_{\mathbf{k}}$  for scattering starting at the outer FERMI sheet (B2). Both figures are shown separately in the Appendix. Additionally, an analysis of the orbital character of initial and final states, to predict smaller or larger relaxation times, as suggested in Ref. [33], fails for the particular case of Pb as well since all states around the FERMI energy are dominated by p-type orbital character.



**Figure 7.** The state-dependent relaxation times  $\tau_{\mathbf{k}}$  for the bands B1 and B2 as well as the next higher band are shown (open circles). Starting from  $\tau_{\mathbf{k}}$ , the energy-dependent  $\tau$  is given calculated by an arithmetic mean value (light blue line) and an adaptive smearing method (black line). Further details are given in the text.

After the detailed investigation of relaxation times in single states  $\mathbf{k}$  at the FERMI energy, the energy dependence of  $\tau$  is investigated. The latter allows to perform accurate transport calculations, which are a step beyond the constant relaxation time

approximation (cRTA), and which we will call energy relaxation time approximation (ERTA).

Figure 7 demonstrates the approach we are using to obtain an energy-dependent relaxation time from a  $\mathbf{k}$ -dependent one. Each open circle corresponds to a relaxation time in state  $\mathbf{k}$  and related energy  $\epsilon_{\mathbf{k}}$ . Since we are interested in  $\tau(E)$ , we compute the arithmetic mean value (AMV) of the scattering rates. The inverse quantity,  $\tau_{\text{AMV}}(E)$  is shown as a solid light blue line. However, the result depends on the width of the energy interval and is rather jagged [||](#). The latter does not affect the results of the electrical conductivity but strongly influences the calculation of the thermopower due to its sensitivity to the slope of the transport distribution function at the FERMI energy. Therefore we use an adaptive smearing method to smoothen the arithmetic mean values (solid black line). The smearing is done with adaptive gaussians of certain widths, which are related to the slope of  $\tau_{\text{AMV}}$ . Here we distinguish between three segments. One includes the peak at the FERMI energy and the signatures slightly above in energy (I) and the other two consist of the remaining parts below (II) and above (III) the first one [¶](#).

This scheme allows us to obtain a band-resolved energy-dependent relaxation time. Evidently one can see that the relaxation time of band B1 is larger compared to B2. This holds for every temperature at every energy because the magnitude of  $\tau$  is mainly given by  $\mathcal{H}(b, f)$ . Additionally, the distribution functions  $b$  and  $f$  are responsible for the low-temperature peaks in  $\tau(E)$  at  $E_F$ . These peaks originate from the decreasing scattering phase space for phonons at temperatures below the DEBYE temperature ( $\Theta_D \approx 95\text{K}$ ), since phonons with longer wavevectors are frozen out and the number of scattering events is drastically reduced. The little bump around 100 meV above  $E_F$  marks the bottom of the next higher band and the relaxation time decreases above this energy due to the additional electronic scattering channels.

The temperature has no significant impact on the functional behaviour of  $\tau(E)$  apart from  $E_F$  and only determines its magnitude (see fig. 8). However, the shape of  $\tau$  near the FERMI energy strongly depends on  $T$  as discussed before. Especially width and slope of the peak at  $E_F$  are important for the calculation of the thermopower. Having this in mind we will distinguish between the following approximations for the relaxation time. First of all we apply a relaxation time approximation, which is constant in energy but depends on temperature and can be either band-dependent, bd-cRTA( $T$ ), or not, cRTA( $T$ ). The values are estimated from  $\tau(E)$  at the FERMI energy for each temperature separately. Next, we use a common approximation of  $\tau$ , including the density of states  $\tau_{\text{DOS}}(E, T) = A(T)/\text{DOS}(E)$ . Here  $A(T)$  is temperature-dependent. Finally, we calculate the transport properties with an energy- and temperature-dependent relaxation time based on a state dependency, as shown in fig. 8.

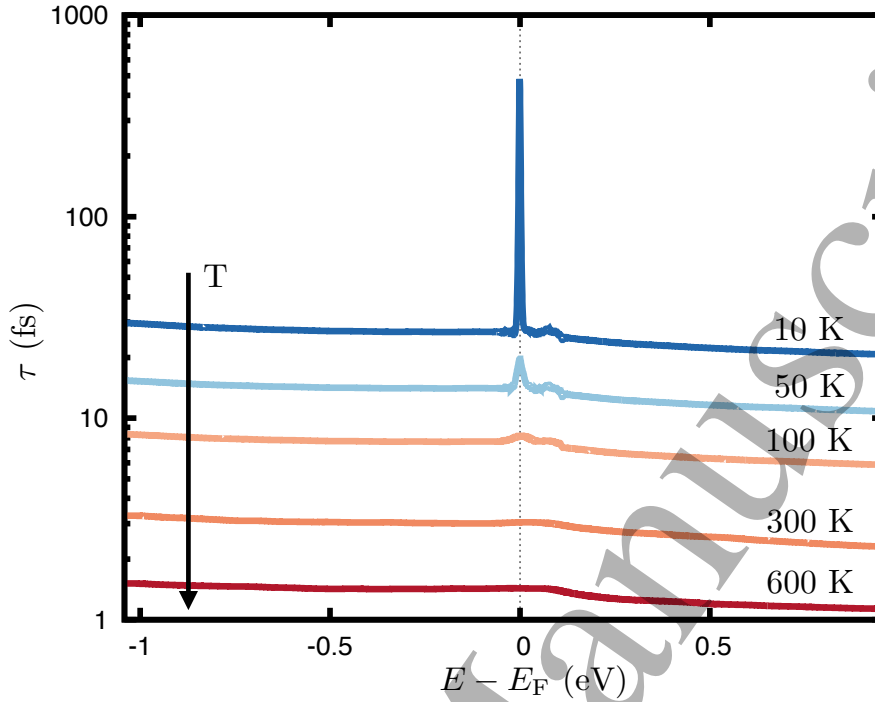
We obtain the electrical conductivity and thermopower within the BOLTZMANN transport theory and the use of generalized transport coefficients

$$\mathcal{L}^{(n)}(\mu, T) = \int dE \Sigma(E) \cdot (E - \mu)^n \left( -\frac{\partial f^0(\mu, T)}{\partial E} \right)_{E_k=E}, \quad (9)$$

where  $\Sigma$  is the transport distribution function (TDF) introduced by MAHAN and SOFO[\[47\]](#) here explicitly accounting for the el-ph transport relaxation time  $\tau^{\text{tr}}$ .

[||](#) Further details are shown in the Appendix

[¶](#) The used smearing values are listed in the Appendix.

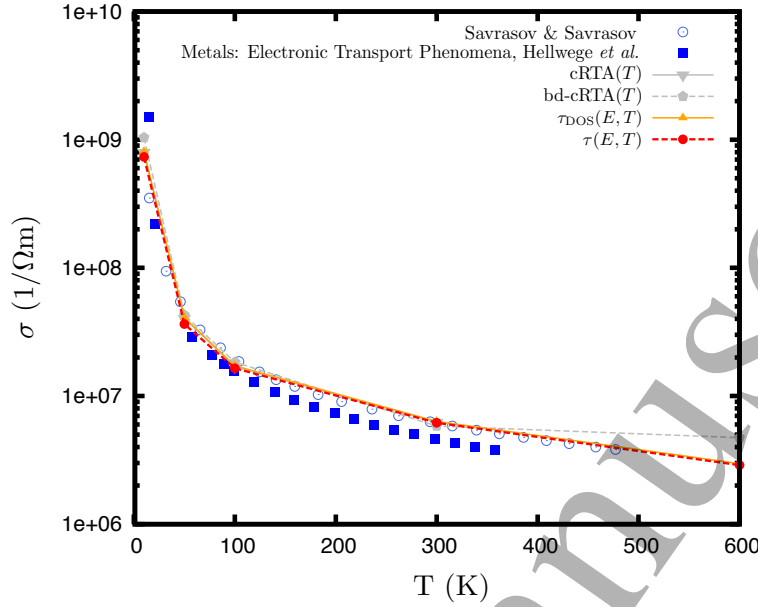


**Figure 8.** Energy-dependent relaxation times are shown for several temperatures from 10K (blue line) to 600K (red line).  $\tau$  is decreasing with increasing temperature as indicated by the black arrow. The peak at  $E_F$  is characteristic for temperatures below  $\Theta_D$  and originates from a freeze-out of long-wavevector phonons and a decreased scattering phase space.

The calculated electrical conductivities within the before mentioned relaxation time approximations agree very well with published experimental and theoretical values (fig. 9). While comparing the used approximations basically no difference can be found and even the temperature-dependent cRTA gives acceptable results. The reason for this is given by the integrand of eq. (10). Here, the electrical conductivity is proportional to the zeroth moment,  $\sigma(\mu, T) \approx \mathcal{L}^{(0)}$  and the important integration range is determined by the energy width of the derivative of the FERMI -DIRAC distribution function, which is in the order of several  $k_B T$ . Within the approximations for  $\tau$  there is almost no difference in the integrand around  $E_F$ .

The situation is different for the diffusive thermopower, as  $S$  is proportional to  $\mathcal{L}^{(1)}(\mathcal{L}^{(0)})^{-1}$  and the specific functional behaviour of  $\Sigma$  nearby  $E_F$  is crucial and changes whether one uses  $\tau(T)$ ,  $\tau_{DOS}(E, T)$  or  $\tau(E, T)$ . In the first two cases, the slope in the energy of the TDF does not change with temperature, only the absolute values are affected by  $T$ . The obtained thermopower within these approximations is almost linear in  $T$  and can not reproduce the experimental data for  $T < \Theta_D$  (see fig. 8, grey/orange solid and grey dashed lines). Nevertheless, they fit quite well at temperatures far above  $\Theta_D$ , which could be expected since all additional features in  $\tau(E, T)$  around  $E_F$  arising from low temperatures are neglected anyway (see fig. 7) and approximations considering the whole phonon spectrum are reliable, as all phonon states are occupied.



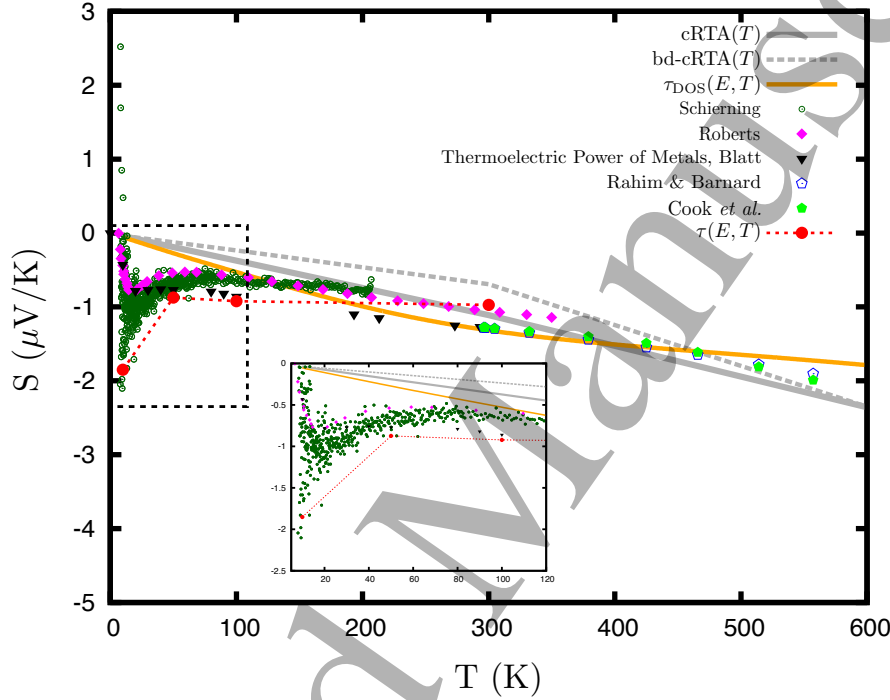


**Figure 9.** Calculated electrical conductivity of lead. The electron-phonon interaction is included within several approximations (lines with points). The results are compared to experimental [2] and theoretical [43] data (closed squares and open circles).

If we include the energy-dependent relaxation time  $\tau(E, T)$  the enhanced thermopower at  $T < \Theta_D$  can be very well described. Since we use the standard approach to solve the BOLTZMANN equation with electron-phonon interaction, i.e. phonons are treated within equilibrium[52], the experimentally observed enhancement of  $S$  is not or at least not solely caused by the phonon-drag effect. The last is usually the explanation for an increased thermopower in low-doped semiconductors but might only partially contribute to an enhanced thermopower in metals. In fact, the peaked asymmetric structure of  $\tau(E, T)$  at low temperatures stemming from an explicit description of the electron-phonon interaction gives rise to an additional contribution to the thermopower even in the diffusive part, which then qualitatively reproduces the measured thermopower. These findings agree well with the qualitative description of an enhanced absolute thermopower  $S_{\text{el-ph}} \propto S_0(1 + \lambda)$  at low temperatures.

Finally we want to comment, that no explicit investigations on the impact of the electron-phonon interaction on the thermal transport properties, e.g. the lattice thermal conductivity, have been carried out within this manuscript. Overall, we expect a minor influence of electron-scattering onto the phonon transport in simple metals like Pb on basis of the following considerations. In general the lattice part of the total thermal conductivity in metals is found to be in the order of a few 1-2% [20]. A suppression of the lattice thermal conductivity in heavily doped Si due to electron-phonon scattering was recently described by combining anharmonic phonon scattering and electron-phonon scattering via Matthiessens rule and subsequently solving a Phonon-Boltzmann equation in single-mode-approximation [27]. Here the reduction was found to be in the order of a few 10% at very high charge carrier concentrations.

In a prototype metal like Pb, this would nevertheless lead to reduction of less than 1% of the total thermal conductivity. The other part of the total thermal conductivity, i.e. the electronic thermal conductivity, is solely determined by the Wiedemann-Franz law via the electrical conductivity  $\sigma$  and the Lorenz function  $L$  [18]. At increasing high charge carrier concentrations the impact of electron-phonon-scattering onto the Lorenz function was found to be small and decreasing [9]. Hence one can conclude that for simple metals, at inherently high charge carrier concentrations, an impact of electron-phonon scattering onto the phonon transport properties is negligible.



**Figure 10.** The calculated thermopower of lead including electron-phonon interaction within several approximations (lines and lines with points) is compared to a variety of measured values (different types of points) [44, 42, 4, 41, 7]. While the relaxation time approximations can not reproduce the experimental data at low temperatures, the energy- and temperature-dependent  $\tau$  describes them very well.

#### 4. Summary

We presented a scheme to calculate the influence of the electron-phonon interaction onto several transport related properties like coupling strength, linewidth and relaxation time based on *ab initio* methods. We explicitly investigated the  $\mathbf{k}$ -dependent structure of  $\tau$  at the FERMI energy and explained its anisotropic character in bulk Pb. We obtained an energy-dependent relaxation time, which we used to calculate the electrical conductivity and thermopower. A comparison with various relaxation time approximations shows no significant difference for the electrical conductivity but revealed the need of at least  $\tau(E, T)$  to reproduce the increased

thermopower at low temperatures, i.e.  $T < \Theta_D$ .

## Acknowledgments

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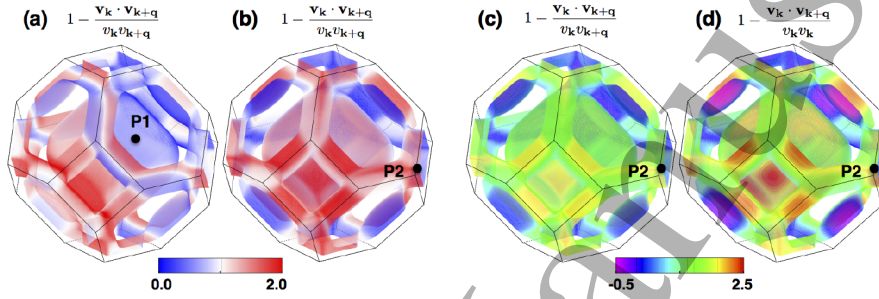
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## Appendix A. Efficiency factor in transport calculations

Figure A1 shows the efficiency factor

$$1 - \frac{\mathbf{v}_k \cdot \mathbf{v}_{k'}}{|\mathbf{v}_k| |\mathbf{v}_{k'}|} \quad (\text{A.1})$$

along with a common approximation in denominator given by  $|\mathbf{v}_k|^2$  instead of  $|\mathbf{v}_k| |\mathbf{v}_{k'}|$ . Considering a system with an isotropic and spherical FERMI surface, i.e. Li or Na, the efficiency factor would reduce to the common term  $(1 - \cos(\mathbf{k}, \mathbf{k}'))$ , which is a reasonable approximation in these system. Nevertheless this approximation completely fails in systems with an anisotropic or multi-sheeted FERMI surface.



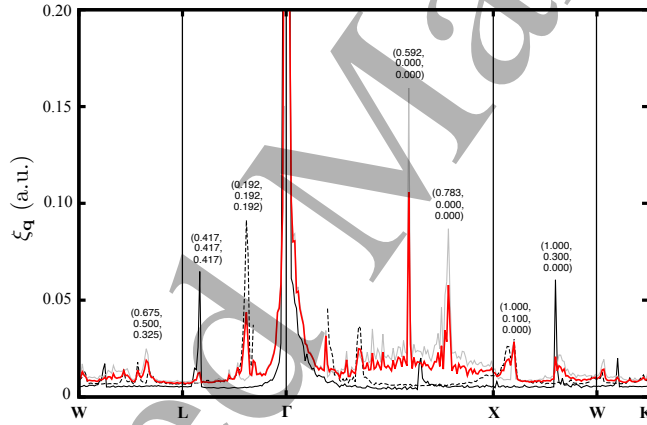
**Figure A1.** Illustration of the efficiency factor, which is used for computing the transport relaxation time  $\tau_k^{\text{tr}}$  or transport coupling constant  $\lambda_k^{\text{tr}}$  in lead. The efficiency factor is shown for a single initial state coupled to all final states via phonons with wave vector  $\mathbf{q}$ . Initial states are P1 (a) and P2 (b)-(d). (c) and (d) shows the difference between the correct efficiency factor and a slightly different version, which is sometimes found in the literature. It is clearly seen, that the latter yields results, which are outside the value range  $[0, 2]$ .

## Appendix B. The electronic nesting function

The nesting function [22]

$$\xi_{\mathbf{q}} = \frac{1}{N} \sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}'m} - E_F) \delta(\epsilon_{\mathbf{k}n} - E_F) \propto \oint \frac{dL_{\mathbf{k}}}{|\mathbf{v}_{\mathbf{k}} \times \mathbf{v}_{\mathbf{k}'}|} \quad (\text{B.1})$$

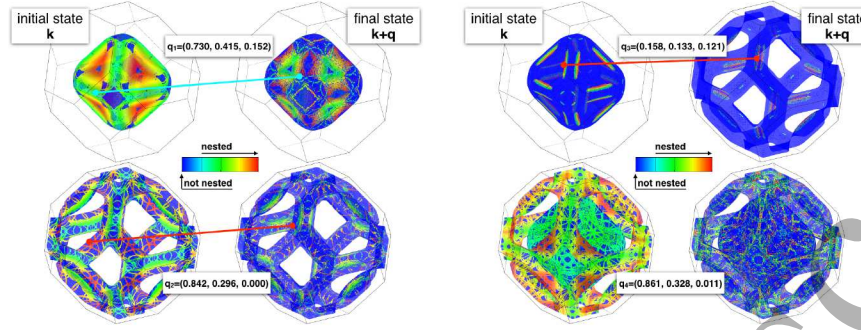
as a part of the FERMI surfaced averaged ÉLIASHBERG spectral function is shown in fig. B1. This quantity indicates phonons from a geometrical point-of-view, which might be important for the correct description of certain properties with respect to the electron-phonon interaction. Phonons with large or diverging nesting values connect parallel orientated parts of the FERMI surface, where the velocities of  $\mathbf{k}$  and  $\mathbf{k}' = \mathbf{k} + \mathbf{q}$  are collinear. This feature is peculiarly pronounced at  $\mathbf{q} = \mathbf{0}$ , where the velocities of initial and final state are equal. Looking at each FERMI sheet separately (solid black (grey) line),  $\xi_{\mathbf{q}}$  maximizes at different wave vectors, according to the geometry of sheets, for example  $\mathbf{q}_{\text{B1}}^{\text{intra}} = (0.417, 0.417, 0.417)$  or  $\mathbf{q}_{\text{B2}}^{\text{intra}} = (0.592, 0.0, 0.0)$ . Combining intra- and interband transitions (red line) leads to a drastical reduction of some peaks ( $\mathbf{q}_{\text{B1}}^{\text{intra}}$ ) while others remain dominant ( $\mathbf{q}_{\text{B2}}^{\text{intra}}$ ). These nesting vectors can be identified via certain cuts through the FERMI surface and are linked to KOHN anomalies [8].



**Figure B1.** Nesting function  $\xi_{\mathbf{q}}$ . The solid black (gray) line corresponds to intraband transitions in the inner (outer) FERMI sheet, while the dashed black line refers to interband transitions. The total nesting function for the whole FERMI surface, without distinguishing between intra- and interband transitions, is given in red. In each case the divergence at  $\mathbf{q} = \mathbf{0}$  is obvious due to collinear velocities  $\mathbf{v}_{\mathbf{k}}$  and  $\mathbf{v}_{\mathbf{k}+\mathbf{q}}$ . Some nesting vectors with larger nesting values are denoted, but the highest values are obtained for vectors not lying on a high-symmetry line, see figure B2.

Besides this more educational investigation of phonons along a high-symmetry line, other wave vectors in the full phonon spectra provide larger nesting values up to a factor of 7 (see fig. B2). This is especially the case for separated intra- and interband transitions. The figures in B2 show connected initial and final states via the phonon with the largest nesting (same color). If the phonon couples more than two states only the pair with the highest contribution to  $\xi_{\mathbf{q}}$  is shown. As one can



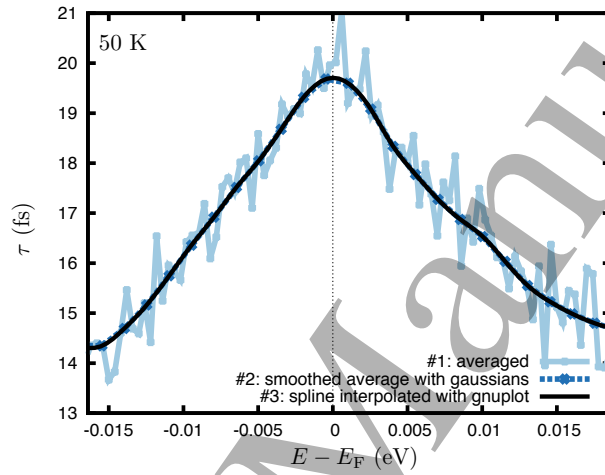


**Figure B2.** Nested electronic states via certain phonons highlighted at the Fermi surface. Same color of the initial and final state marks a nested pair, except for blue, which displays the bare Fermi surface. Only states connected by the phonon with the highest nesting value  $\xi_q$  are shown. If  $q$  connects more than one pair only the pair with the highest weight is given. Left: Intraband transitions mediated by  $q_1$  (top, inner sheet,  $\xi_{q_1} \approx 0.495$ ) and  $q_2$  (bottom, outer sheet,  $\xi_{q_2} \approx 0.19$ ). Right: Interband transitions via  $q_3$  (top,  $\xi_{q_3} \approx 0.219$ ). The bottom figure shows the result, taking both transition types into account ( $\xi_{q_4} \approx 0.108$ ).

see, the largest nesting vectors lie off the high-symmetry line. Adding up intra- and interband transitions (bottom right) results in a nesting vector  $q_4$ , which provides only a slightly larger nesting than  $q_{B2}$ . However the visualization of connected states is much more complicated in this case and therefore not shown in the figure.

### Appendix C. Details of the calculation of $\tau(E, T)$ from $\tau(\mathbf{k}, T)$

Figure C1 shows the calculation of  $\tau(E, T)$  from  $\tau_{\mathbf{k}}$ , which is given in fig. 7 in the main text, in more detail. The arithmetic mean value  $\tau^{\text{AMV}}$  is obviously not smooth but enters directly into the generalized transport coefficients. Because the calculation of the thermopower is really sensitive to the slope of the transport distribution function, which is hardly affected by the relaxation time,  $\tau^{\text{AMV}}$  has to be smoothen before the calculation. After the smoothing with adaptive gaussians, we further use a spline interpolation. Nevertheless, this last step does not change the result significantly. The parameters for the gaussians are listed in table C1.



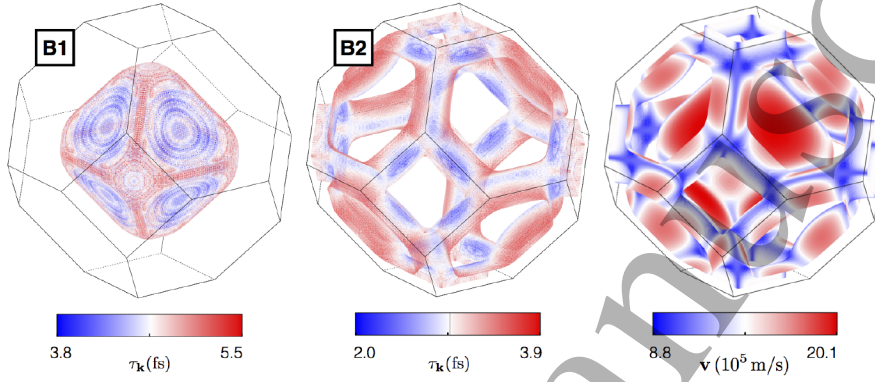
**Figure C1.** A more detailed picture of the energy-dependent relaxation time at 50K, which is shown in figure 7 in the main text. The energy window is much smaller around the FERMI energy to show the jagged arithmetic mean value  $\tau^{\text{AMV}}$ , which was calculated from state-dependent  $\tau_{\mathbf{k}}$ .

**Table C1.** Used smearing values in the gaussians to smoothen the calculated arithmetic mean values of the relaxation time. Smearing is given in meV.

segment	10K	50K	100K	300K	600K
I	2	2	20	50	50
II/III	50	50	50	50	50

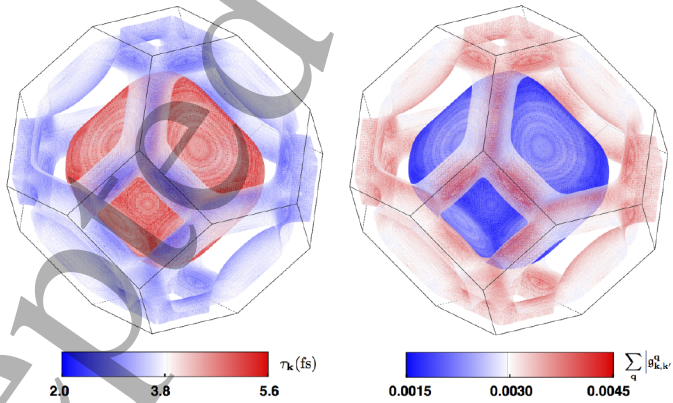
#### Appendix D. Comparison of carrier velocity, relaxation time and matrix elements

Figure D1 indicates, that there is probably no clear correlation between the carrier velocity  $\mathbf{v}_{\mathbf{k}}$  of the initial state and its relaxation time  $\tau_{\mathbf{k}}$ . If the initial state is at the inner FERMI sheet (B1), it holds  $\tau_{\mathbf{k}} \propto 1/v_{\mathbf{k}}$ , while the opposite is true for an initial state at the outer sheet (B2), where it is  $\tau_{\mathbf{k}} \propto v_{\mathbf{k}}$ .



**Figure D1.** Left and middle: State-dependent relaxation time  $\tau_{\mathbf{k}}$  for initial states at the inner FERMI sheet B1 and the outer FERMI sheet B2. Take care of the different scales. Right: Carrier velocity in Pb.

In contrast to the FERMI velocity, the investigation of the summed up matrix elements  $\sum_{\mathbf{q}} |\mathbf{g}|^2$  for each initial state can explain larger or smaller relaxation times, which can be seen in figure D2. Mustafa *et. al* showed this already for simple metals [33] but it seems to be reasonable in more complicated metals as well.



**Figure D2.** Left: State-dependent relaxation time  $\tau_{\mathbf{k}}$  for initial states at the FERMI surface without distinguishing between intra- and interband scattering. Right: Matrix elements for the same initial states summed over phonons.